IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:
Takayuki Araki et al.

Art Unit: 1795

Application No. 09/700,185

Examiner: RUTHKOSKY, MARK

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For: Material for solid polyelectrolyte suitable for use in fuel cell

Commissioner for Patents
PO Box 1450
Alexandria, VA 22313-1450
Sir:

DECLARATION UNDER 37 C.F.R.Section 1.132

I, Tadashi INO, do hereby declare that:

1. I am a Japanese citizen, residing at Yodogawa Seisakusho, DAIKIN INDUSTRIES, LTD., 1-1, Nishihitotsuya, Settsu-shi, Osaka 5660044 Japan.

2. I graduated from Faculty of Engineering, Kyoto University in March 1984. I also graduated from the graduate school of Engineering Department of Molecular Engineering, Kyoto University, and received a master's degree in Molecular Engineering in 1986.

3. I began my employment with Daikin Industries Limited, the assignee of the above-identified application, in 1986. Since 1986, I have been engaged in the research and development of fluoropolymer materials.

4. I am familiar with the subject matter of above-identified application as well as the disclosures in the cited reference.

5. In order to demonstrate the differences between the present invention and

the prior art teachings, I have conducted the following experiments.

Experiment

(1) Synthesis of Sulfonic Acid Fluoride Group-Containing Fluoropolymer Chain Corresponding to Segment A

Following the procedure of Synthesis Example 1 in the present specification, a sulfonic acid fluoride group-containing fluoropolymer chain corresponding to Segment A was synthesized.

A 500 ml stainless steel autoclave equipped with a stirrer, a thermometer and a pressure gauge was charged with 225 g of pure water, 25 g of an emulsifier represented by Formula (4)

$CF_3CF_2CF_2OCF(CF_3)COONH_4$ (4),

5.0 g of a monomer containing sulfonic acid fluoride groups (hereinafter referred to briefly as "PFSF") represented by Formula (5)

$CF_2=CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$ (5),

and 0.1 g of a diiodine compound $I-(CF_2)_4-I$. After fully purging the system with nitrogen gas, the internal temperature was maintained at 60°C with stirring, and tetrafluoroethylene gas was supplied so that the internal pressure became 2.0 kgf/cm^2G. Then, 5.0 ml of 0.1% aqueous solution of ammonium persulfate (APS) was injected under nitrogen pressure to initiate a reaction. The pressure decreased as the polymerization reaction proceeded, and when the pressure decreased to 1.5 kgf/cm^2G, tetrafluoroethylene gas was supplied to increase the pressure to 2.0 kgf/cm^2G. The decrease and increase of the pressure were repeated. From the start of the polymerization, while continually supplying tetrafluoroethylene gas, 2.5 g of the sulfonic acid fluoride group-containing monomer (PFSF) was injected each time 1.7 g of tetrafluoroethylene gas was consumed, to continue polymerization. Tetrafluoroethylene gas was supplied 9 times (22.5 g) in total. When 17 g of tetrafluoroethylene gas was consumed, the supply was stopped. Then, the autoclave was cooled, and unreacted monomers

were released, giving 293 g of an aqueous dispersion having a solid concentration of 13.4%.

One gram of the aqueous dispersion was taken, and frozen for coagulation. After thawing, the coagulation product was washed with water and vacuum-dried to obtain a white polymer.

The dried white polymer was completely soluble in perfluorobenzene, HCFC-225 or like fluorine-containing solvent.

^{19}F-NMR analysis revealed that the monomer composition of the polymer was TFE/PFSF=78.3/21.7 mol%. The polymer had a molecular weight per sulfonic acid group (equivalent weight ((EW)) of 806.

<u>(2) Production of B-A-B Block Polymer</u>

<u>(2-1) Synthesis of Block 1 (EW=879, Segment A : Segment B = 91.7 : 8.3 (wt. %))</u>
Following the procedure of Example 1 in the present specification as described below, sulfonic acid fluoride group-containing Segment A (EW=806) obtained in (1) above was copolymerized with tetrafluoroethylene/perfluoropropylvinyl ether to produce Block 1 (B-A-B block polymer) with an EW of 879 and a Segment A : Segment B ratio of 91.7 : 8.3 (wt. %).

The same 500 ml autoclave as used in (1) above was charged with 120 g of the aqueous dispersion (concentration: 13.4%) of the sulfonic acid fluoride group-containing fluoropolymer (Segment A, EW=806) obtained in (1) above, and 120 g of pure water. After fully purging the system with nitrogen gas, the internal temperature was maintained at 60°C with stirring.

A gaseous monomer mixture of tetrafluoroethylene/perfluoropropylvinyl ether (PPVE) (97/3 mol%) previously prepared in a cylinder, was injected so that the internal pressure became 7.5 kgf/cm^{2}G. Then, 3 ml of 0.1% aqueous solution of ammonium persulfate (APS) was injected under nitrogen pressure to initiate a reaction. The pressure decreased as the polymerization reaction proceeded, and when the pressure decreased to 7.0 kgf/cm^{2}G, the above gaseous monomer mixture was supplied to increase the pressure to 7.5 kgf/cm^{2}G. The decrease and increase of the pressure were repeated, while supplying the

tetrafluoroethylene/PPVE gaseous monomer mixture. When 1.5 g of the gaseous monomer mixture was consumed from the start of the polymerization, the supply was stopped. Then, the autoclave was cooled and unreacted monomers were released, giving 240 g of an aqueous dispersion having a solid concentration of 7.3%. The percentage of Segment B to the whole polymer was calculated from the increase in amount of the polymer:

{(Amount of polymer obtained by second polymerization) – (Amount of polymer used in second polymerization)}/(Amount of polymer obtained by second polymerization) x 100 = 8.3%.

The aqueous dispersion was frozen for coagulation, and the coagulated polymer was washed with water and dried to obtain a white polymer.

The obtained B-A-B block polymer had an EW of 879 and a Segment A : Segment B ratio of 91.7 : 8.3 (wt.%).

(2-2) Synthesis of Block 2 (EW=946, Segment A : Segment B = 85.2 : 14.8 (wt. %))

Following the procedure of Example 1 in the present specification as described below, sulfonic acid fluoride group-containing Segment A (EW=806) obtained in (1) above was copolymerized with tetrafluoroethylene/perfluoropropylvinyl ether to produce Block 2 (B-A-B block polymer) with an EW of 946 and a Segment A : Segment B ratio of 85.2 : 14.8 (wt. %).

The same 500 ml autoclave as used in (1) above was charged with 120 g of the aqueous dispersion (concentration: 13.4%) of the sulfonic acid fluoride group-containing fluoropolymer (Segment A, EW=806) obtained in (1) above, and 120 g of pure water. After fully purging the system with nitrogen gas, the internal temperature was maintained at 60°C with stirring.

A gaseous monomer mixture of tetrafluoroethylene/perfluoropropylvinyl ether (PPVE) (97/3 mol%) previously prepared in a cylinder, was injected so that the internal pressure became 7.5 kgf/cm^{2}G. Then, 3 ml of 0.1% aqueous solution of ammonium persulfate (APS) was injected under nitrogen pressure to initiate a reaction. The pressure decreased as the polymerization reaction proceeded,

and when the pressure decreased to 7.0 kgf/cm^2G, the above gaseous monomer mixture was supplied to increase the pressure to 7.5 kgf/cm^2G. The decrease and increase of the pressure were repeated, while supplying the tetrafluoroethylene/PPVE gaseous monomer mixture. When 3.0 g of the gaseous monomer mixture was consumed from the start of the polymerization, the supply was stopped. Then, the autoclave was cooled and unreacted monomers were released, giving 242 g of an aqueous dispersion having a solid concentration of 7.8%. The percentage of Segment B to the whole polymer was calculated from the increase in amount of the polymer:

{(Amount of polymer obtained by second polymerization)– (Amount of polymer used in second polymerization)}/(Amount of polymer obtained by second polymerization) x 100 = 14.8%.

The aqueous dispersion was frozen for coagulation, and the coagulated polymer was washed with water and dried to obtain a white polymer.

The obtained B-A-B block polymer had an EW of 946 and a Segment A : Segment B ratio of 85.2 : 14.8 (wt.%).

(3) Film Preparation

Following the procedure of Example 3 in the present specification, each of the sulfonic acid fluoride ($-SO_2F$) group-containing segmented fluoropolymers Block 1 and Block 2 obtained in (2) above and the commercial product Nafion EW 1100 was placed in a mold of 100 mm diameter, and the mold was mounted on a pressing machine set at 350°C. After 20-minute preliminary heating, compression molding was performed at 70 kg/cm^2 for 1 minute to obtain 0.2 mm thick films.

The obtained films containing $-SO_2F$ groups were treated in the same manner as in Example 3 of the present specification as described below, for hydrolysis and drying.

Hydrolysis of $-SO_2F$ groups

Each of the $-SO_2F$ group-containing films (Block 1, Block 2, and Nafion EW 1100) obtained in (2) above was fully impregnated with an aqueous solution of 25%

NaOH, and allowed to stand at 90℃ for 8 hours. The solid was then impregnated with an aqueous solution of 6N HCl at room temperature for 4 hours, followed by drying at 110°C for 6 hours.

(4) Calculation of modulus in tension (dyn/cm^2) from measurement of dynamic viscoelasticity

Following the procedure of Example 3 in the present specification, each of the dry films (Block 1, Block 2, and Nafion EW 1100) obtained in (3) above was immersed in boiling pure water, and allowed to stand for 30 minutes to incorporate water.

Immediately after incorporation of water, a rectangle (about 35 mm x 5 mm) was cut out from each film and set on a viscoelasticity measuring device RSA-2 (a product of Rheometric) to measure the modulus in tension at a frequency of 1 Hz at various temperatures. Fig. A shows the results.

Fig. A reveals that Block 1 (EW=879, Segment A : Segment B = 91.7 : 8.3 (wt.%)), in which the proportion of Segment B containing no sulfonic acid fluoride group is smaller than that defined in Claim (Segment A : Segment B = 30 : 70 to 90 : 10 (wt. %)), has a lower modulus in tension than the commercial product Nafion EW 1100.

In contrast, Block 2 (EW=946, Segment A : Segment B = 85.2 : 14.8 (wt.%)), in which the Segment A : Segment B ratio is within the range of 30 : 70 to 90 : 10 (wt.%), has a higher modulus in tension than Block 1 and the commercial product Nafion EW 1100, at high temperatures of 110°C or more, demonstrating greatly improved mechanical strength.

Since Block 2 (EW=946) has a lower molecular weight per sulfonic acid group (EW) (i.e., has a smaller proportion of a structural reinforcing element PTFE) than the commercial product Nafion EW 1100, it is usually presumed that the mechanical strength of Block 2 (EW=946) is lower than that of the commercial product Nafion EW 1100.

However, by forming a block with a Segment A : Segment B ratio of 30 : 70 to 90 : 10 (wt.%), a material for a solid polyelectrolyte was obtained that has higher

mechanical strength than the commercial product Nafion EW 1100 containing a large proportion of the structural reinforcing element PTFE.

Further, Block 2 (EW=946) of the present invention has high ion conductivity, since it has a lower molecular weight per sulfonic acid group (EW) (i.e., contains a greater proportion of sulfonic acid groups as the ion conducting component of the polymer) than the commercial product Nafion EW 1100.

(5) Conclusion

It can be presumed that when the proportion of sulfonic acid groups in a polymer is increased to enhance ion conductivity (i.e., when the EW is decreased), the proportion of PTFE, which contributes to high mechanical strength, is decreased, thereby reducing the mechanical strength of the polymer.

In the present invention, however, a material for a solid polyelectrolyte can be obtained that has higher mechanical strength than the commercial product Nafion EW 1100 containing a large proportion of the structural reinforcing element PTFE and that retains high ion conductivity, by forming a block with a Segment A : Segment B ratio of 30 : 70 to 90 : 10 (wt.%).

6. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of any patent issued on this application.

Date: April, 22, 2008

By: Tadashi Ino

Tadashi INO